Inorganica Chimica Acta, 210 (1993) 193–201

Multinuclear (^{31}P, ^{195}Pt) magnetic resonance and electrospray mass spectrometric studies of the reactions between platinum bis(dithiolates) and two potentially tetradentate phosphine ligands

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(Received March 12, 1993; revised May 12, 1993)

Abstract

The reactions of platinum(II) bis(dithiolates) $Pt(S-S)_2$ ((S-S) = $S_2P(OEt)_2$ (dtp), S_2CO^nPr (xan), S_2CNEt_2 (dtc)) with two potentially tetradentate phosphine ligands have been investigated by multinuclear magnetic resonance spectroscopy and electrospray mass spectrometry (ESMS). The phosphines used were $P(CH_2CH_2PPh_2)_3$ (P_3P') and $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$ ($P_2P'_2$). ^{31}P and ^{195}Pt NMR spectroscopies show that P_3P' reacts in dichloromethane solution with $Pt(dtp)_2$ and $Pt(xan)_2$ to give five-coordinate $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-}S\text{-}S)]^+$ and with $Pt(dtc)_2$ to give a temperature dependent mixture of $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtc})]^+$ and $[(\eta^3\text{-}P_3P')Pt(\eta^2\text{-dtc})]^+$. All these formulations were confirmed by observation of the intact ions in the ES mass spectra directly from the solutions. $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-xan})]^+$ slowly reacts with the free xan ion to give the dithiocarbonate complex $(\eta^3\text{-}P_3P')Pt(\eta^2\text{-}S_2CO)$. The pendant phosphine in $[(\eta^3\text{-}P_3P')Pt(\eta^2\text{-dtc})]^+$ undergoes various chemical reactions such as methylation and reaction with sulfur, and the cation behaves as a monodentate phosphine towards $Pt(dtp)_2$ to give $[(\eta^1\text{-dtp})(\eta^2\text{-dtp})Pt(\eta^1\text{-}\mu^2\text{-}\eta^3\text{-}P_3P')Pt(\eta^2\text{-dtc})]^+$ which was fully characterised by multi-NMR spectroscopy and confirmed by observation of the intact ion by ESMS. $P_2P'_2$ reacts with $Pt(dtp)_2$ to give $[(P_2P'_2)Pt]^{2+}$, but with $Pt(xan)_2$ and $Pt(dtc)_2$ the products are $[(\eta^4\text{-}P_2P'_2)Pt(\eta^1\text{-}S\text{-}S)]^+$, but the xanthate complex slowly de-alkylates to give $(\eta^3\text{-}P_2P'_2)Pt(\eta^2\text{-}S_2CO)$. The identities of the cationic $P_2P'_2$ species in solution were confirmed by direct observation of the intact ion by ESMS.

Introduction

The reactions between platinum(II) bis(dithiolates), $Pt(S-S)_2$ (S-S = $S_2P(OR)_2$, S_2COR, S_2CNR_2, etc.) and monodentate phosphines have been thoroughly investigated by Stephenson [1–5] and Fackler [6, 7] and their co-workers who established the general reactions

$$Pt(S\text{-}S)_2 + PR_3 \longrightarrow (PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S)$$

$$(PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S) + PR_3 \longrightarrow [(PR_3)_2Pt(\eta^2\text{-}S\text{-}S)]^+ + [S\text{-}S]^-$$

More recently we have used multinuclear magnetic resonance spectroscopy to extend these studies to reactions of platinum dithiolates with potentially bidentate and tridentate phosphine based ligands [8–12]. In this paper we further extend these investigations to reactions of platinum dithiolates with the two isomeric tetraphosphines tris(2-diphenylphosphinoethyl)phosphine [13] ($P(CH_2CH_2PPh_2)_3$, P_3P') and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane [14] ($Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$, $P_2P'_2$).

King *et al.* [15] investigated the reactions of K_2PtCl_4 with both phosphines and produced compounds of the type $[Pt(\eta^4\text{-}P_4)][PF_6]_2$ while Tau *et al.* [16] reacted $Pt(cod)Me_2$ (cod = 1,4-cyclooctadiene) with the phosphines to give fluxional complexes of the type $(\eta^2\text{-}P_4)PtMe_2$. In an extensive series of papers [17–23] Brüggeller has thoroughly investigated P_3P' and $P_2P'_2$ complexes of Pt(II) with hydride, chloride and monodentate phosphine co-ligands using multi-NMR methods and a number of five-coordinate compounds have been characterised.

Electrospray mass spectrometry (ESMS) provides a new method of transferring pre-existing ions from solution to the gas phase. The transfer is very soft and causes minimal fragmentation. The ES technique has been developed mainly by Fenn and co-workers [24–26]

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0020-1693/93/$6.00

and its most spectacular successes have been in the area of mass spectrometry of large bio-molecules [27–29] where its use is expanding exponentially [30], but to date there are few applications of the technique to inorganic chemistry.

We have been investigating the application of ESMS to inorganic and organometallic systems [31–35], and a feature of these studies is that the intact ions are always observed, often as the only significant peak. In particular, we have shown that cationic derivatives of the platinum dithiolates with phosphine ligands are readily observed by ESMS [36]. The term 'intact ion' is used to refer to an ion transferred from solution to the gas phase without any change, in contrast to molecular ion which refers to an ion formed by loss of an electron from a neutral species.

In this paper we report studies on the reactions of platinum(II) dithiolates with P_3P' and $P_2P'_2$ using both multi-NMR and ESMS methods.

Experimental

Platinum dithiolates were prepared as described previously [10, 11] whilst P_3P' and $P_2P'_2$ were commercial samples (Strem). Analyses were performed by Chemical and Microanalytical Services P/L (CMAS), Geelong and data are given in Table 1.

Most reactions were initially studied *in situ* in the NMR tube. Many of the products were subsequently isolated by reaction on a larger scale in dichloromethane solution, similar to the preparations of $[(P\text{-}P)Pt(dtc)]^+$ (P-P = diphosphine) [9]. After evaporation of the solvent the products were recrystallised from dichloromethane/n-hexane.

NMR spectra were recorded using a JEOL FX 100 spectrometer, ^{31}P at 40.32 MHz and ^{195}Pt at 21.32 MHz with external ^7Li lock. External references were 85% H_3PO_4 and 1 M H_2PtCl_6 in conc. HCl; high frequency positive convention is used for chemical shifts.

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Tech, Altrincham, Ches., UK) with a water/methanol/acetic acid (50:50:1%) mobile phase. The compounds were dissolved in dichloromethane (2 mM) and a portion of this solution was diluted 1:10 with methanol. The diluted solution was injected directly into the spectrometer via a Rheodyne injector with a 10 μl loop using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporisation nozzle of the electrospray ion source at a flow rate of 3 μl min^{-1}. Voltages at the first skimmer electrode (B1) were varied between 100 V and the minimum possible to retain a stable ion jet. This varies from time to time but is usually in the range 25–30 V. Increasing the B1 voltage enhances the formation of daughter ions by collisional activation within the ion source. In addition, ions of a particular *m/z* value (i.e. the most intense peak in an isotopic mass distribution) can be selected and passed through a collision cell into a second mass analyser. At low ion energies and in the absence of introduced gas in the collision cell, the stabilities of the mass selected precursor ions can be investigated. Collisional activated decomposition (CAD) mass spectra of the selected ions were obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

Results and discussion

All reactions were initially performed *in situ* in an NMR tube at temperatures specified in the text. Many of the compounds were subsequently isolated and upon subsequent dissolution in dichloromethane they gave NMR spectra identical to those obtained *in situ*. Peaks in the ES mass spectra are identified by the most intense peak in the isotopic mass distribution and in all cases there was excellent agreement between the experimental and calculated isotopic mass distribution.

Reactions of platinum dithiolates with P_3P'

All NMR data for compounds containing P_3P' are given in Table 2. The ^{31}P NMR spectrum of P_3P' itself consists of a doublet at δ −13.1 and a quartet at δ −17.5 [37]. Equimolar amounts of $Pt(S_2P(OEt)_2)_2$ $(Pt(dtp)_2)$ and P_3P' were mixed in dichloromethane at −90 °C. The ^{31}P NMR spectrum at −30 °C shown in

TABLE 1. Analytical data

Compound	C (%)		H (%)		Melting point (°C)
	Found	Calc.	Found	Calc.	
$[(P_3P')Pt(xan)][BPh_4]$	63.5	63.7	5.33	5.23	165
$[(P_3P')Pt(dtc)][BPh_4]$	63.7	64.0	5.80	5.41	83
$[(P_3P')PtCl]Cl$	51.6	51.7	4.59	4.60	262

TABLE 2. ^{31}P and ^{195}Pt NMR data for the P_3P' derivatives in dichloromethane solution

Compound	$\delta(^{31}P)$ (ppm)	$\delta(^{195}Pt)$ (ppm)	$J(Pt, P)$ (Hz)	Temperature (°C)
P_3P'	-13.1s			
	-17.5s			
$[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtp})]^+$	124.5s	-4780qdd	$^1J=2140$	-90
	96.4q		$^2J=105$	
	26.8d		$^1J=2640$	
			$^3J(P, P)=24$	
$[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-xan})]^+$	119.1s	-4800qd	$^1J=2040$	20
	21.8s		$^1J=2610$	
$[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtc})]^+$	95.2s	-4925dq	$^1J=2670$	50
	22.0s		$^1J=2040$	
$[(\eta^3\text{-}P_3P')Pt(\eta^2\text{-dtc})]^+$	99.2s	-5000td	$^1J=2695$	-80
	41.7s		$^1J=3020$	
	-15.0s			
$[(\eta^3\text{-}P_3P')Pt(\eta^2\text{-}S_2CO)]^+$	98.5d	-5060td	$^1J=2725$	20
	41.5s		$^1J=2835$	
	26.3d		$^3J(P, P)=55$	
$[(\eta^4\text{-}P_3P')PtCl]^+$	119.7s	-4360qd	$^1J=2525$	20
	26.7s		$^1J=2580$	
$[(\eta^3\text{-}(PMe)P_2P')Pt(\eta^2\text{-dtc})]^+$	100.4d	-4970td	$^1J=2740$	20
	39.9s		$^1J=2960$	
	25.1d		$^3J(P, P)=54$	
$[(\eta^2\text{-}(PS)P_2P')Pt(\eta^2\text{-dtc})]^+$	95.5d	-4970d	$^1J=2740$	20
	43.0d		$^3J(P, P)=54$	
	39.5s		$^1J=3000$	
$[(\eta^3\text{-}(PS)_2PP')Pt(\eta^2\text{-dtc})]^+$	50.3m	-4835dd	$^1J=3050$	20
	48.3s		$^1J=3110$	
	43.6s			
$[(dtp)_2Pt(\eta^1\text{-}\mu^2\text{-}\eta^3\text{-}P_3P')Pt(dtc)]^+$	97.4s	-5000td	$^2J=350$	-80
	96.3s	-4510ddd	$^1J=2720$	
	92.7s		$^2J=130$	
	41.5s		$^1J=2950$	
	6.2s		$^1J=3720$	
	5.2s			

s = singlet, d = doublet, m = multiplet, dd = doublet of doublets, dq = doublet of quartets, qd = quartet of doublets, td = triplet of doublets, ddd = doublet of doublets of doublets, qdd = quartet of doublets of doublets.

Fig. 1(a) consists of two singlets at δ 124.5 and 111.4, a quartet at δ 96.4 and a doublet at δ 26.8; both the multiplets have $^3J(P, P)=24$ Hz. All the signals have ^{195}Pt satellites except the singlet at δ 111.4 which is assigned to free [dtp]$^-$ [8]. The quartet is assigned to the phosphorus atom of a monodentate dithiophosphate ligand since the coupling constant to platinum is small ($^2J(Pt, P)=105$ Hz). Typically, monodentate dithiophosphates show coupling constants to platinum of about 100 Hz while bidentate dithiophosphates have coupling constants in the range 300–400 Hz [5, 8]. The other two signals which have intensities in the ratio 1:3 are due to the phosphorus atoms of P_3P' and there is no free ligand or pendant phosphorus, since there is no resonance around δ -15. At -90 °C the spectrum is essentially the same, except that the signals are broadened due to viscosity effects. However, the ^{195}Pt NMR spectrum is sharper at low temperatures and the spectrum at -90 °C, shown in Fig. 1(b), consists of a quartet of doublets of doublets. It is entirely consistent with the ^{31}P NMR spectrum and both indicate the formation of $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtp})][dtp]$ in solution. The P_3P' ligand has a tripod structure [13] which suggests a trigonal bipyramidal geometry for $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtp})]^+$ as shown in Structure 1. Similar structures have been characterised for $[(\eta^4\text{-}P_3P')PtCl]^+$ [38] and $[(\eta^4\text{-}P_3P')PtH]^+$ [17] and their NMR parameters compare well with those for the proposed $[(\eta^4\text{-}P_3P')Pt(\eta^1\text{-dtp})]^+$. When the solution is allowed to stand for three days, both the ^{31}P and the ^{195}Pt NMR spectra indicate that two new compounds are present in solution and that none of the original material remains, but after seven days only one of the species remains. NMR spectra characterise the final product as $[(\eta^4\text{-}P_3P')PtCl]^+$ [38], but the intermediate has not been identified.

The ES mass spectrum of a solution containing equimolar quantities of $Pt(dtp)_2$ and P_3P' is shown in Fig. 2(a). The major peak at *m/z* 1050 is due to the

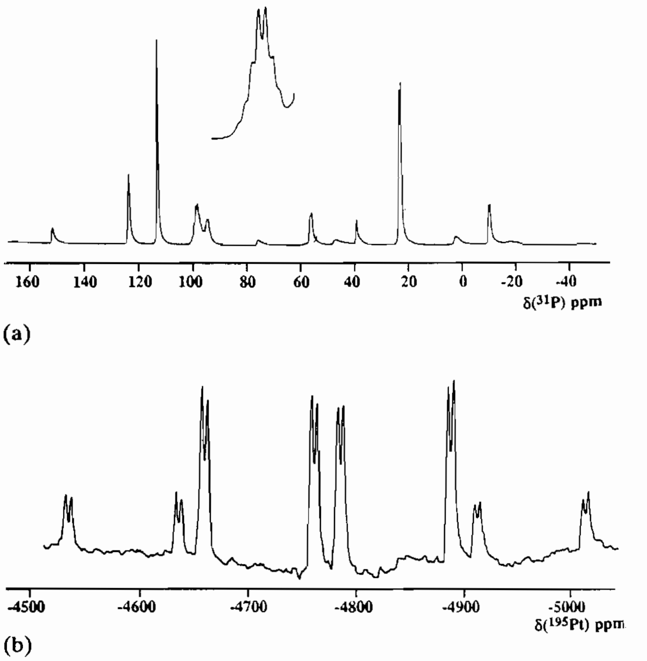
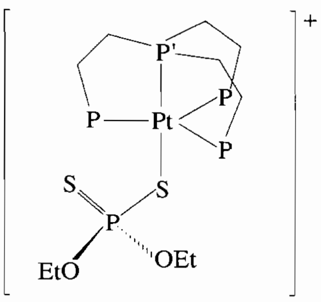


Fig. 1. NMR spectra of a dichloromethane solution containing equimolar proportions of Pt(dtp)$_2$ and P$_3$P′ (a) ^{31}P at −30 °C, (b) ^{195}Pt at −90 °C.



Structure 1.

intact ion [(P$_3$P′)Pt(dtp)]$^+$ and the two smaller peaks at higher *m/z* values are due to phosphine oxide derivatives formed within the ion source. Formation of phosphine oxides is common in ESMS [32, 34]. The CAD MS (Fig. 2(b)) of selected ions of *m/z* 1050 shows daughter ions at *m/z* 897, 865, 712, 684 and 652. The daughter at *m/z* 897 is [(P$_3$P′)PtS]$^+$ with only the S atom of the dtp ligand remaining and further loss of sulfur gives the ion at *m/z* 865. The daughter ions at *m/z* 712 and 684 show progressive degradation of the P$_3$P′ ligand giving [P′(CH$_2$CH$_2$PPh$_2$)$_2$(CH$_2$=CH$_2$)PtS]$^+$ and [P′(CH$_2$CH$_2$PPh$_2$)$_2$PtS]$^+$ fragments. The daughter ion at *m/z* 652 has no S atom attached to platinum. All ESMS data are summarised in Table 3.

The reaction between equimolar quantities of Pt(S$_2$CO^{n}Pr)$_2$, Pt(xan)$_2$ and P$_3$P′ in dichloromethane gives a product whose ^{31}P NMR spectrum is two singlets (1:3) with ^{195}Pt satellites and the ^{195}Pt NMR spectrum is a quartet of doublets. Chemical shifts and coupling constants are very similar to those of [(η^4-P$_3$P′)Pt(dtp)]$^+$ (Table 2), leading to the conclusion that a similar trigonal bipyramidal cation [(η^4-P$_3$P′)Pt(xan)]$^+$ is formed.

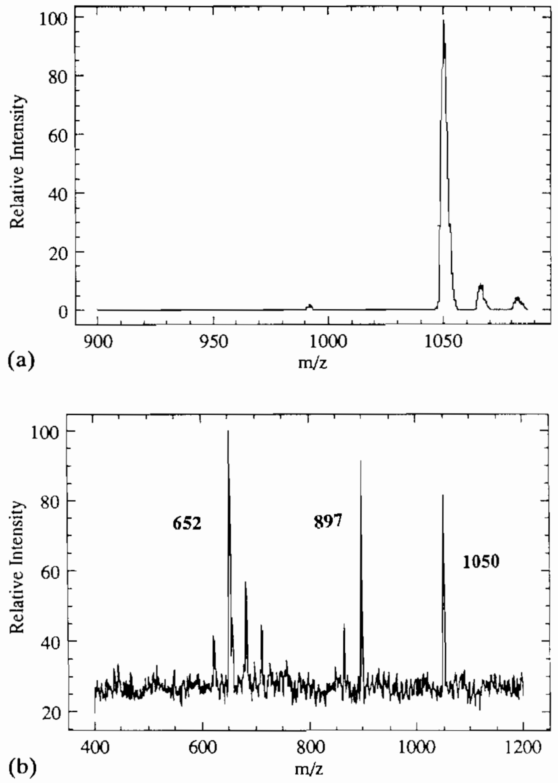


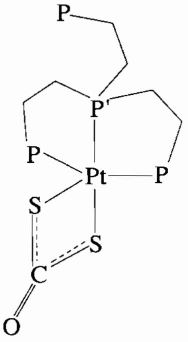
Fig. 2. (a) ES mass spectrum of a solution containing equimolar proportions of Pt(dtp)$_2$ and P$_3$P′, (b) CAD MS of ions of *m/z* 1050.

When the solution is allowed to stand for a week, a second compound is detected together with unreacted [(η^4-P$_3$P′)Pt(xan)]$^+$. The ^{31}P NMR spectrum of the new complex consists of a doublet at δ 98.5 and a singlet at δ 41.5, each with ^{195}Pt satellites, and a doublet at δ 26.3 without satellites (1:2:1). The ^{195}Pt NMR spectrum is a triplet of doublets. All of the information is consistent with the well established [12] de-alkylation of the coordinated xanthate by the ionic xanthate to give a derivative of dithiocarbonate. The data also reveals tridentate coordination of the P$_3$P′ ligand. The complex is assumed to be five-coordinate because [S$_2$CO]$^{2-}$ is known to be a strong chelating ligand [11] and also because this is the first example of displacement of one of the phosphine groups from platinum. It is impossible on the basis of these results to distinguish between trigonal bipyramidal and square pyramidal geometries, but as the other compounds are unequivocally trigonal bipyramidal, Structure 2 is suggested for (η^3-P$_3$P′)Pt(η^2-S$_2$CO). The signal due to the uncoordinated phosphine is well removed from that of

TABLE 3. ESMS and CAD MS data

Compound	ESMS (*m/z*)	CAD MS (*m/z*)
[(η^4-P$_3$P′)Pt(dtp)][dtp]	[(P$_3$P′O$_2$)Pt(dtp)]$^+$ (1082) [(P$_3$P′O)Pt(dtp)]$^+$ (1066) [(P$_3$P′)Pt(dtp)]$^+$ (1050)	[(P$_3$P′)PtS]$^+$ (897) [(P$_3$P′)Pt]$^+$ (865) [(P$_2$P′(CH$_2$=CH$_2$))PtS]$^+$ (712) [(P$_2$P′)PtS]$^+$ (684)^a [(P$_2$P′)Pt]$^+$ (652)^a
[(η^4-P$_3$P′)Pt(xan)][BPh$_4$]	[(P$_3$P′O)Pt(xan)]$^+$ (1016) [(P$_3$P′)Pt(xan)]$^+$ (1000)	[(P$_3$P′)PtS]$^+$ (897) [(P$_3$P′)Pt]$^+$ (865) [(P$_2$P′)Pt]$^+$ (652)^a
[(η^4-P$_3$P′)Pt(dtc)][dtc]	[(P$_3$P′O)Pt(dtc)]$^+$ (1029) [(P$_3$P′)Pt(dtc)]$^+$ (1016)	[(P$_2$P′)PtS]$^+$ (684)^a [(P$_2$P′)Pt]$^+$ (652)^a
[(dtp)$_2$Pt(μ-P$_3$P′)Pt(dtc)][PF$_6$]	[(P$_3$P′)Pt$_2$(dtp)$_2$(dtc)]$^+$ (1578)	
[(η^4-P$_2$P′$_2$)Pt(dtp)][dtp]	[(P$_2$P′$_2$)Pt(dtp)]$^+$ (1050) [(P$_2$P′$_2$)Pt]$^+$ (865) [(P$_2$P′$_2$)Pt]$^{2+}$ (432.5)	[(P$_2$P′$_2$)PtS]$^+$ (897) [(P$_2$P′$_2$)Pt]$^+$ (865) [(PP′$_2$)PtS]$^+$ (684)^b [(PP′$_2$)Pt]$^+$ (652)^b [(PCH$_2$)Pt]$^+$ (240)
[(η^4-P$_2$P′$_2$)Pt(xan)][xan]	[(P$_2$P′$_2$O$_3$)Pt(xan)]$^+$ (1048) [(P$_2$P′$_2$O$_2$)Pt(xan)]$^+$ (1032) [(P$_2$P′$_2$O)Pt(xan)]$^+$ (1016) [(P$_2$P′$_2$)Pt(xan)]$^+$ (1000) [(P$_2$P′$_2$)Pt(OAc)]$^+$ (924) [(P$_2$P′$_2$)PtCl]$^+$ (900) [(P$_2$P′$_2$)Pt]$^{2+}$ (432.5)	
[(η^4-P$_2$P′$_2$)Pt(dtc)][dtc]	[(P$_2$P′$_2$)Pt(dtc)]$^+$ (1014) [(P$_2$P′$_2$)Pt(OAc)]$^+$ (924) [(P$_2$P′$_2$)Pt]$^{2+}$ (432.5)	
[(P$_2$P′$_2$)Pt][dtp]$_2$	[(P$_2$P′$_2$)Pt]$^{2+}$ (432.5)	[(P$_2$P′$_2$-Ph)Pt]$^{2+}$ (394)^c [PPh$_2$]$^+$ (185)

^{a}P$_2$P′ = P(CH$_2$CH$_2$PPh$_2$)$_2$. ^{b}PP′$_2$ = Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh. ^{c}P$_2$P′$_2$-Ph = Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPhCH$_2$CH$_2$PPh.



Structure 2.

the free ligand but is not shifted sufficiently to be assigned to a phosphine oxide.

The ES mass spectrum of [(P$_3$P′)Pt(xan)]BPh$_4$ consists essentially of a single peak at *m/z* 1000 which is due to the intact ion [(P$_3$P′)Pt(xan)]$^+$, but there is also a much weaker peak at *m/z* 1016 due to [(P$_3$P′O)Pt(xan)]$^+$. The tandem CAD MS shows only two daughter ions at *m/z* 897 and 652 assigned to [(P$_3$P′)PtS]$^+$ and [(P(CH$_2$CH$_2$PPh$_2$)$_2$Pt]$^+$, respectively.

The reaction between equimolar quantities of Pt(S$_2$CNEt$_2$)$_2$, Pt(dtc)$_2$ and P$_3$P′ gives species whose NMR spectra vary with temperature between 50 and −80 °C. Above room temperature the spectra were recorded in chloroform and at lower temperatures in dichloromethane, and at 20 °C spectra are identical in both solvents. At 50 °C the ^{31}P NMR spectrum consists of two singlets at δ 95.2 and 22.0, (1:3) both with ^{195}Pt satellites. The corresponding ^{195}Pt NMR spectrum is a doublet of quartets. Chemical shifts and coupling constants are similar to those for the corresponding dithiophosphate and xanthate derivatives (Table 2) and the data suggest that at 50 °C the species in solution is [(η^4-P$_3$P′)Pt(η^1-dtc)]$^+$. Between 50 and about −60 °C the system is fluxional but sharp spectra are once again observed at −80 °C. At this temperature the ^{31}P NMR spectrum consists of three singlets at δ 99.2, 41.7 and −15.0 (1:2:1) and the lower frequency signal is without ^{195}Pt satellites, and its position suggests that it is due to a pendant phosphorus. The ^{195}Pt NMR spectrum is a triplet of doublets, confirming that only three phosphorus atoms are coordinated to platinum at low temperature. Although we have no direct evidence on the coordination of the dithiocarbamate ligand, it is assumed to be bidentate, and the compound is formulated as [(η^3-P$_3$P′)Pt(η^2-dtc)]$^+$, since the NMR parameters are similar to those of (η^3-P$_3$P')Pt(η^2-S$_2$CO).

Thus, the two species identified at 50 and −80 °C are structural isomers of [(P$_3$P')Pt(dtc)]$^+$ and the fluxional behaviour arises because of the equilibrium

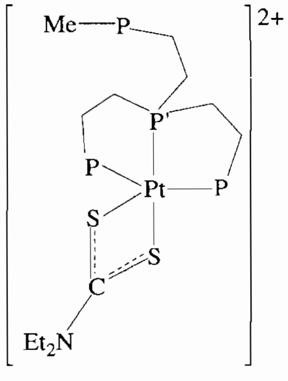
$$[(\eta^4\text{-P}_3\text{P}')\text{Pt}(\eta^1\text{-dtc})]^+ \rightleftharpoons [(\eta^3\text{-P}_3\text{P}')\text{Pt}(\eta^2\text{-dtc})]^+$$

There are six potential donor atoms competing for five coordination sites and the two ligands have almost equal chelating abilities. We have shown [11] that dtc is a stronger chelating ligand than dtp and xan and these dithiolates cannot compete successfully with P$_3$P' for the coordination sites so only [(η^4-P$_3$P')Pt(η^1-S-S)]$^+$ (S-S = dtp, xan) are observed. In contrast, [S$_2$CO]$^{2-}$ is a stronger chelating ligand than dtc, so with this dithiolate only (η^3-P$_3$P')Pt(η^2-S$_2$CO) is observed. The cation [(P$_3$P')Pt(dtc)]$^+$ was isolated as its tetraphenylborate salt and its empirical formula was confirmed by elemental analysis (Table 1).

The ES mass spectrum of a solution containing equimolar quantities of Pt(dtc)$_2$ and P$_3$P' consists essentially of only one peak at *m/z* 1013 which is due to the intact ion [(P$_3$P')Pt(dtc)]$^+$, but there is also a very weak peak at *m/z* 1029 due to phosphine oxide formation. Although ESMS confirms the identity of the cation in solution, it cannot provide the detailed structural information available from NMR spectroscopy. The CAD MS is similar to those for the other dithiolate cations, and the data are summarised in Table 3.

Reactions of [(P$_3$P')Pt(dtc)]$^+$

A chloroform solution containing [(P$_3$P')Pt(dtc)]$^+$ was reacted with a small excess of MeI. The ^{31}P NMR spectrum shows two doublets at δ 100.4 and 25.1 and a singlet at δ 39.9 (1:1:2). The doublet at lower frequency does not have ^{195}Pt satellites and is in the region associated with phosphonium salts [39]. The ^{195}Pt NMR spectrum is a triplet of doublets and all the data are consistent with the formulation [(η^3-(PMe)P$_2$P')Pt(η^2-dtc)]$^{2+}$ (Structure 3). The NMR data compare well with those for [(η^3-P$_3$P')Pt(η^2-dtc)]$^+$ (Table 2), but the methylated complex is not fluxional at room temperature because there is now no competition between the ligands since only five potential donor atoms are available for coordination.



Structure 3.

A sample of [(P$_3$P')Pt(dtc)](BPh$_4$) in dichloromethane was reacted at room temperature with a slight excess of elemental sulfur. After one day, both the ^{31}P and ^{195}Pt NMR spectra at 20 °C indicated the presence of two non-fluxional species in solution. For one compound, the data are very similar to those for [(η^3-P$_3$P')Pt(η^2-dtc)]$^+$ except that the signal due to pendant phosphorus is replaced by a signal at δ 43.0, which is typical for a P=S group [40]. The compound is identified as [(η^3-(PS)P$_2$P')Pt(η^2-dtc)]$^+$ (similar to Structure 3). The second compound has NMR data very similar to that of the square planar cation [(η^2-dpe)Pt(η^2-dtc)]$^+$ (dpe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) [9] except for a ^{31}P NMR signal at δ 43.8 in the region associated with P=S groups. This product is identified as square planar [(η^2-(PS)$_2$PP')Pt(η^2-dtc)]$^+$. NMR data for these compounds are summarised in Table 2.

In an effort to use the pendant phosphorus in [(η^3-P$_3$P')Pt(η^2-dtc)]$^+$ as a monodentate phosphine ligand, the cation was reacted with Pt(dtp)$_2$ at −80 °C in dichloromethane solution. The ^{31}P NMR spectrum of this solution consists of four singlets (1:1:2:1) and an apparent doublet (intensity 1) (Table 2). Two of the singlets at high frequency have coupling constants to platinum of 350 and 130 Hz, indicating one monodentate and one bidentate dtp ligand. The remaining signals all have platinum satellites and large coupling constants and, importantly, there is no signal around δ −15 which could be assigned to a pendant phosphine. The ^{195}Pt NMR spectrum at −80 °C is much more definitive and is shown in Fig. 3. It consists of a doublet of doublets of doublets, at higher frequency, and a triplet of doublets indicating the presence of two non-equivalent platinum environments. The multiplet at lower frequency is very

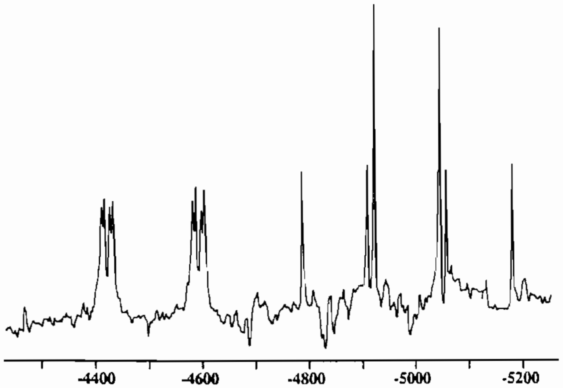


Fig. 3. ^{195}Pt NMR spectrum at −80 °C of a dichloromethane solution containing equimolar quantities of [(P$_3$P')Pt(dtc)][BPh$_4$] and Pt(dtp)$_2$.

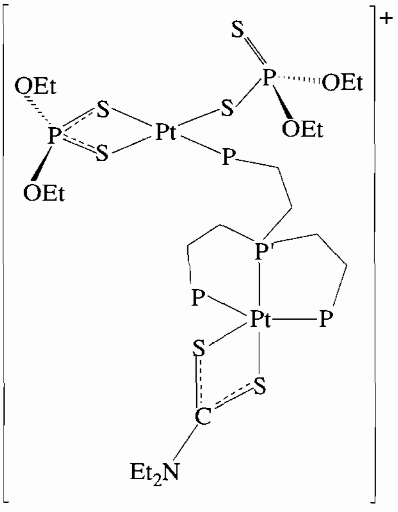
similar to that described previously for $[(\eta^3\text{-}P_3P')Pt(\eta^2\text{-}dtc)]^+$ itself, and the doublet of doublets of doublets is very similar in both chemical shift and coupling constants to the ^{195}Pt NMR spectrum of $(PPh_3)Pt(\eta^1\text{-}dtp)(\eta^2\text{-}dtp)$ [5]. On the basis of these spectra the compound in solution is formulated as the binuclear complex $[(\eta^1\text{-}dtp)(\eta^2\text{-}dtp)Pt(\eta^1\text{-}\mu^2\text{-}\eta^3\text{-}P_3P')Pt(\eta^2\text{-}dtc)]^+$ (Structure 4). The positions of the resonances in the ^{31}P NMR spectrum are also consistent with this formulation, the only anomaly being that the resonance at δ 5.7 is an apparent doublet. This signal is assigned to the single phosphorus directly bonded to the dtp platinum, but we believe there are two geometrical isomers or conformers giving rise to slightly different chemical shifts for this atom so the signal is actually two singlets. The non-equivalence probably arises from a restricted rotation, but we are not able to identify the exact cause.

$[(dtp)_2Pt(P_3P')Pt(dtc)][PF_6]$ was isolated and its ES mass spectrum was examined in a dichloromethane/methanol (1:10) solution. Remarkably, the positive ion mass spectrum showed only one peak at *m/z* 1578 which corresponds to the intact ion $[(P_3P')Pt_2(dtp)_2(dtc)]^+$.

Reactions of platinum dithiolates with $P_2P'_2$

$P_2P'_2$ is a linear tetraphosphine ligand which contains two sets of two phosphorus atoms in different environments. Its ^{31}P NMR spectrum consists of two doublets at δ −13.6 and −17.1 [41]. The ligand has two diasteroisomers, *meso* and the *chiral* form [42], which have been separated (approximately 2:1 mixture) from a commercial sample [43], although we were unable to detect two isomers in the sample used for our experiments.

NMR data for all the complexes containing $P_2P'_2$ are given in Table 4. When equimolar quantities of $Pt(dtp)_2$ and $P_2P'_2$ are mixed in dichloromethane at −50 °C the ^{31}P NMR spectrum consists of a singlet (no satellites) at δ 110.8 and two doublets with ^{195}Pt satellites. The ^{195}Pt NMR spectrum at −50 °C is a triplet of triplets and the data is consistent with the formation of square planar $[(\eta^4\text{-}P_2P'_2)Pt]^{2+}$ and free dithiophosphate ion. This cation has been reported previously by Brüggeller [19] with similar NMR parameters. If the solution is allowed to stand for a week at room temperature the positions of the resonances and the coupling constants change, although the general appearance of the spectra remains similar. Comparison with published spectra [19] suggests that the product is $[(\eta^4\text{-}P_2P'_2)PtCl]^+$, formed by reaction with the solvent.



Structure 4.

Somewhat surprisingly the ES mass spectrum of a solution containing equimolar quantities of $Pt(dtp)_2$ and $P_2P'_2$ gave two strong peaks at *m/z* 1050 and 432.5. The more intense peak at *m/z* 432.5 is due to the dication $[(P_2P'_2)Pt]^{2+}$ and that at *m/z* 1050 is due to $[(P_2P'_2)Pt(dtp)]^+$. This cation was not observed by NMR spectroscopy, and is presumably formed in the ion source. The tandem CAD MS of *m/z* 1050 ions gave several daughter ions which contain either a sulfur atom or no residue from the dtp ligand with progressive fragmentation of the $P_2P'_2$ ligand being observed, similar to that for the P_3P' complexes. The CAD MS of $[(P_2P'_2)Pt]^{2+}$ gave similar ligand fragmentation and the data are summarised in Table 3.

When equimolar quantities of $Pt(xan)_2$ and $P_2P'_2$ are mixed in dichloromethane at −50 °C the ^{31}P NMR spectrum consists of two equal intensity doublets and the ^{195}Pt NMR spectrum is a rather broad triplet of triplets. This data indicates that all four phosphorus atoms are coordinated to platinum, but the NMR parameters are not the same as those for $[(\eta^4\text{-}P_2P'_2)Pt]^{2+}$. They do however closely match those for $[(\eta^4\text{-}P_2P'_2)PtCl]^+$, so it is proposed that the product is $[(\eta^4\text{-}P_2P'_2)Pt(xan)]^+$. Confirmation of this formulation comes from the ES mass spectrum which shows several peaks including one at *m/z* 1000 due to $[(P_2P'_2)Pt(xan)]^+$. The other peaks are due to phosphine oxide derivatives, similar to those described earlier, $[(P_2P'_2)PtCl]^+$ formed within the ion source from dichloromethane in the solvent, $[\eta^4\text{-}P_2P'_2)Pt(OAc)]^+$ with the acetate being derived from the mobile phase, and $[(P_2P'_2)Pt]^{2+}$. Data are summarised in Table 3.

If the mixture of $Pt(xan)_2$ and $P_2P'_2$ in dichloromethane is allowed to stand for some four weeks the NMR spectra change. The ^{31}P NMR spectrum is now four singlets (1:1:1:1) with the one at lowest frequency being without ^{195}Pt satellites (Table 4). The ^{195}Pt NMR spectrum is a doublet of doublets of doublets and the data are consistent with the formation of $(\eta^3\text{-}P_2P'_2)Pt(\eta^2\text{-}S_2CO))$.

TABLE 4. ^{31}P and ^{195}Pt NMR data for the $P_2P'_2$ derivatives in dichloromethane solution

Compound	$\delta(^{31}P)$ (ppm)	$\delta(^{195}Pt)$ (ppm)	$J(Pt, P)$ (Hz)	Temperature (°C)
$P_2P'_2$	−13.6d −17.1d			20
$[(\eta^4\text{-}P_2P'_2)Pt][dtp]_2$	89.4d 46.4d	−5305tt	$^1J = 2170$ $^1J = 2480$ $J(P, P) = 285$	−50
$[(\eta^4\text{-}P_2P'_2)Pt(\eta^1\text{-xan})][xan]$	78.0d 32.2d	−5200tt	$^1J = 2535$ $^1J = 2420$ $J(P, P) = 290$	−50
$[(\eta^3\text{-}P_2P'_2)Pt(\eta^2\text{-dtc})][dtc]$	87.1s 28.4s 20.2s 16.0s	−5120ddd −5140ddd	$^1J = 2840$ $^1J = 2850$ $^1J = 2800$	−100
$(\eta^3\text{-}P_2P'_2)Pt(\eta^2\text{-}S_2CO)$	92.4s 51.8s 46.9s 19.4s	−5015ddd	$^1J = 2415$ $^1J = 2520$ $^1J = 2585$	20
$[(\eta^4\text{-}P_2P'_2)PtCl]^+$	84.2d 40.6d	−5220tt	$^1J = 2380$ $^1J = 2620$ $J(P, P) = 295$	20
$[(\eta^4\text{-}P_2P'_2)PtI]^+$	78.7d 31.5d	−5315tt	$^1J = 2440$ $^1J = 2600$ $J(P, P) = 335$	20

s = singlet, d = doublet, td = triplet of doublets, tt = triplet of triplets, ddd = doublet of doublets of doublets.

When equimolar amounts of $Pt(dtc)_2$ and $P_2P'_2$ are mixed in dichloromethane the ^{31}P NMR spectrum at −100 °C is four singlets (1:1:1:1) with one at δ 16.0 being without satellites. The ^{195}Pt NMR spectrum at −100 °C is two almost superimposed doublet of doublets of doublets. The data is consistent with the formation of $[(\eta^3\text{-}P_2P'_2)Pt(\eta^1\text{-dtc})]^+$ and the splitting in the ^{195}Pt NMR signals probably arises because the P′ atom linked to the pendant phosphine is chiral. If the temperature is increased the NMR signals broaden, indicating the molecule is fluxional, and these changes are reversible. At 20 °C the ^{31}P NMR spectrum is two broad doublets and the ^{195}Pt NMR spectrum is a broad seven line multiplet (1:2:3:4:3:2:1) suggesting some dynamic equilibrium exists in solution. In this case, however, studies above room temperature could not be conducted by changing the solvent since the NMR spectra in chloroform were different to those in dichloromethane and the processes remain unidentified.

The ES mass spectrum of a freshly prepared mixture of $Pt(dtc)_2$ and $P_2P'_2$ in dichloromethane/methanol gave a relatively weak peak for $[(P_2P'_2)Pt(dtc)]^+$ (*m/z* 1013) together with peaks due to $[(P_2P'_2)Pt]^{2+}$ (*m/z* 432.5) and $[(P_2P'_2)Pt(OAc)]^+$ (*m/z* 924) as well as some additional unidentified signals.

Conclusions

The application of electrospray mass spectrometry to inorganic systems is still in its infancy, and to date most studies have been on well characterised systems which have usually been studied previously by NMR methods. Although we have previously stated our opinion that a combination of the ESMS and multi-NMR methods would be a very powerful approach to the determination of structures in solution, we believe this paper is in fact the first in which the combination has been used to explore new inorganic chemistry. The work described in this paper serves to illustrate the complementary information which the techniques provide and it also highlights the differences in the ease with which that information is obtained. Many of the NMR spectra need to be acquired at low temperature and a considerable number of accumulations were required for some of the ^{195}Pt NMR spectra. However, the data is usually definitive and, importantly in these systems, it can distinguish between different ligand coordination modes. ES mass spectra are acquired at room temperature within a few minutes of sample injection, and even if there are several components in the system undergoing exchange which is fast on the NMR timescale, ESMS will observe them all, provided they are ionic [33–35]. The disadvantage of ESMS is that it cannot distinguish between isomers and different ligand coordination modes.

Following the original studies of Stephenson and Fackler [1–7] on the reactions of platinum(II) bis(dithiolates) with monodentate phosphine ligands, we have investigated their reactions with diphosphines

[8–10], triphosphines [12] and finally tetraphosphines. Throughout the earlier studies with the polydentate phosphines there were significant differences between the reactivities of the three platinum dithiolates, which was formalised by a study of competition reactions [11], and the same differences persist in the reactions with the tetraphosphines. As the number of potential donor atoms on the phosphines increases, competition for coordination to platinum leads to formation of five-coordinate complexes or complete displacement of both dithiolates.

Acknowledgements

We thank La Trobe University for a SCAEF major equipment grant which contributed towards the purchase of the electrospray mass spectrometer, and the Australian Research Council for financial support for platinum chemistry. V.T. thanks the Commonwealth Government for an Australian Postgraduate Research Award.

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